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Electronic Supplementary Information

A first quaternary diamond-like semiconductor with 10−membered LiS_4 rings exhibiting excellent nonlinear optical performances

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CONTENTS

1. Synthesis of Title Compounds

All the starting materials were used as purchased without further purification. In the preparation process, a graphite crucible was added into the vacuum sealed silica tube to avoid the reaction between metal Li and silica tube at the high temperature. Initially, we attempted to prepare the Li_2HgGeS_4 with the ratio of Li:HgS:Ge:S = 2:1:1:3 at the reaction temperature of 700 °C. However, after washed by the N, N−dimethylformamide (DMF) solvent and measured under the single crystal X−ray diffraction test, two new compounds $Li_4HgGe_2S_7$ (main product, ~80%, yellow) and $Li_{1.8}Hg_{1.1}GeS_4$ (a small amount, ~20%, reddish) were interestingly obtained. To further improve the pure phase of $Li_4HgGe_2S_7$, other ratio of reactants and reaction temperatures were used, but only the crystals of $Li_{1.8}Hg_{1.1}GeS_4$ were obtained. Thus, to complete the following measurement of $Li_4HgGe_2S_7$, its measured sample was obtained by roughly hand-picked. Note that this material is stable in air over half one year.

Powder X-ray diffraction (XRD) analysis was measured on a Bruker D2 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) at room temperature. The 2θ range was 10-70° with a step size of 0.02° and a fixed counting time of 1s/step.

2. Structural Refinement and Crystal Data

High quality single-crystal of $Li_4HgGe_2S_7$ was carefully picked and used for data collection with a Bruker SMART APEX II 4K CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) at 296 K. Its structure was solved by direct method and refined using the SHELXTL program package.[1] Multi-scan method was used for absorption correction.[2] Rational anisotropic thermal parameters for all atoms were obtained by the anisotropic refinement and extinction correction. PLATON was also used to check the final structure and no other symmetries were found. Result of single-crystal refinement was given the rational formula "$Li_4HgGe_2S_7$". Detail refinement parameters and data were shown in Table S1, the atomic coordinates, isotropic displacement parameters and bond valence sums (BVS) were shown in Table S2.

3. Property Characterization

UV−vis−Near IR Diffuse-Reflectance and IR Spectroscopy

Diffuse-reflectance spectrum was tested by a Shimadzu SolidSpec-3700DUV spectrophotometer in the wavelength range of 190−2600 nm at room temperature. IR spectra were collected with a Shimadzu IR Affinity-1 Fourier transform infrared spectrometer in wavenumber range from 400 to 4000 cm^{-1} using picked single-crystals mixed with KBr pellets.

Raman Spectroscopy

Hand-picked crystals were firstly put on an object slide, and then a LABRAM HR Evolution spectrometer equipped with a CCD detector by a 532 nm laser was used to record the Raman spectra. The integration time was set to be 10 s.

Thermal Analysis

The thermal analysis was measured on a simultaneous NETZSCH STA 449C thermal analyzer instrument. The crushed crystals were placed in Al_2O_3 crucible, and the temperature was raised from 40 to 1000 °C at 10 °C/min under N_2 atmosphere.

Second-harmonic Generation Measurement

Measured sample was obtained by roughly hand-picked. Unfortunately, we have not prepared the enough sample to complete the phase-matching measurement. Future growth of large-size crystals for $Li_4HgGe_2S_7$ and further relative test evaluation are in progress. By means of the Kurtz and Perry method, powder SHG responses were investigated by a Q-switch laser (2.09 μm, 3 Hz, 50 ns) with ground micro-crystals at 200−250 μm particle size. $AgGaS_2$ single-crystal was also ground and sieved into the same size range as the reference. SHG signal was detected by a digital oscilloscope.

LDT Measurement

Ground micro-crystals sample was used to evaluate the LDT under a pulsed YAG laser (1.06 μm, 10 ns, 10 Hz). Similar sizes of $AgGaS_2$ crystal are chosen as the reference. By adjusting the laser output energy, colour change of the test sample was carefully observed by an optical microscope to determine the LDT.

Theoretical Calculations.

With the plane wave pseudopotential method, the electronic structure of $Li_4HgGe_2S_7$ was performed on density functional theory (DFT).[3] The Perdew-Burke-Ernzerhof (PBE) of Generalized Gradient Approximation (GGA)[4] and the normconserving pseudopotential (NCP) were chosen.[5,6] Kinetic energy cut-offs was set to be 720.0 eV and Monkhorst-Pack *k*-point meshes (5 × 5 × 3) with a density of 0.03 $Å^{-1}$ in the Brillouin zone (BZ) was adopted. The orbital electrons were treated as valence electrons as follows, Li $2s^1$, S $3s^2$ $3p^4$, Ge $4s^2$ $4p^2$, Hg $5d^{10}$ $6s^2$. Other important parameters, such as NLO coefficient and birefringence, were also calculated based on the scissors operators.[7]

4. Figures and Tables

Fig. S1 TG and DSC curves for $Li_4HgGe_2S_7$.

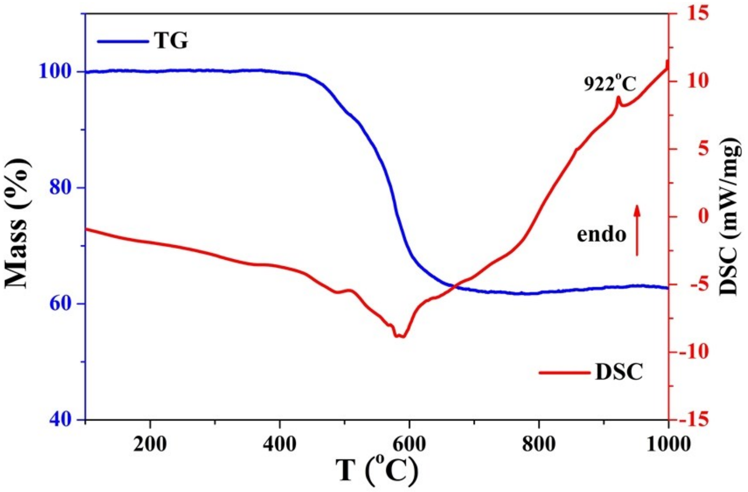
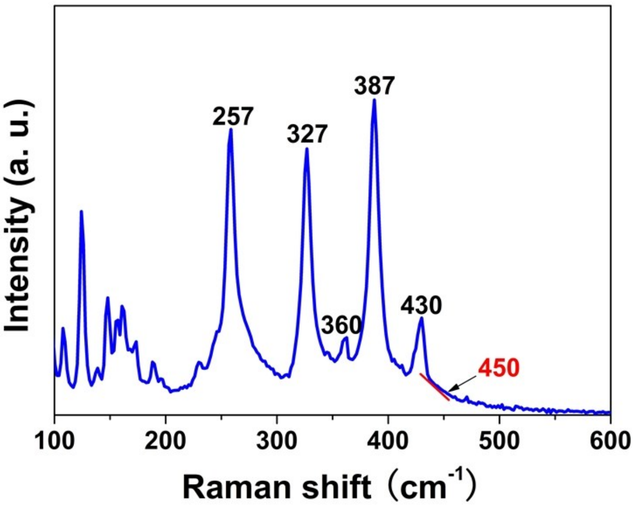
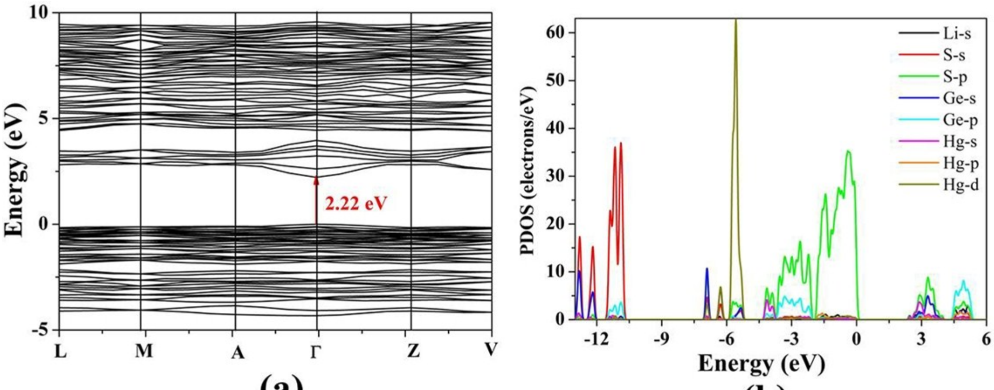


Fig. S2 Raman spectrum of $Li_4HgGe_2S_7$.



Raman spectrum displays strong absorption bands at 430, 387, 360, and 327 cm^{-1} attributed to the characteristic absorptions of Ge−S mode. The bands at around 257 cm^{-1} are attributed to Hg−S bonding interaction, which are also similar to those of other related metal sulfides. Other bands below the 200 cm^{-1} can be attributed to the characteristic absorptions of Li−S mode.

Fig. S3. (a) Band structure and (b) Projected density of states (PDOS) of $Li_4HgGe_2S_7$.



(a) (b)

Fig. S4. SHG−density diagram of $Li_4HgGe_2S_7$. The rainbow represents the activities of the veocc state and veunocc state SHG.

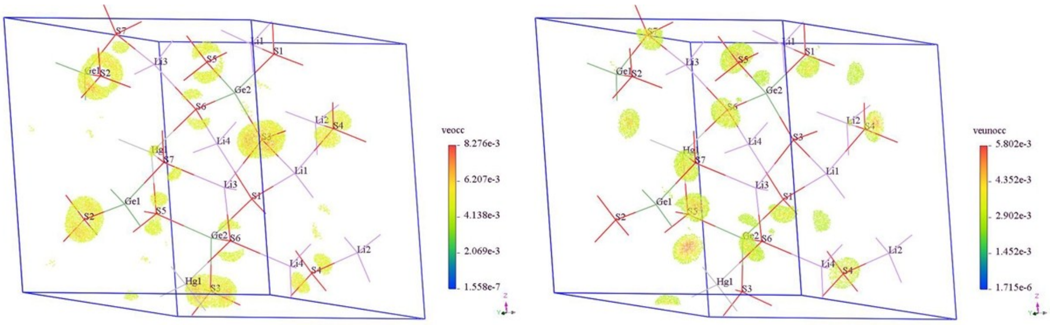


Table S1 Comparison on the critical properties (bandgap and NLO coefficient) for several of (d^{10} elements and Mn)-containing metal sulfide DLSs.

Materials	Bandgap (eV)	NLO coefficient (pm/V)	Ref.
$HgGa_2S_4$	**2.84**	**31.5**	8, 9, 12
$CdGa_2S_4$	3.44	15.83	10, 11, 12
$ZnGa_2S_4$	3.60	11.92	10, 12
$Ag_4CdGe_2S_7$	2.45	14.51	13, 12
$Ag_4HgGe_2S_7$	**2.11**	**23.07**	13, 12
Li_2CdGeS_4	3.15	22.5	14
Li_2MnGeS_4	3.07	6.6	15
$Li_4HgGe_2S_7$	**2.75**	**19.5**	**This work**
$Li_4CdGe_2S_7$	4.23	4.29	12

Table S2 Structure refinement and crystal data for $Li_4HgGe_2S_7$.

Empirical formula	$Li_4HgGe_2S_7$
formula weight	597.95
crystal system	*Monoclinic*
space group	*Cc*
a (Å)	16.876(2)
b (Å)	6.7764(8)
c (Å)	10.1613(13)
	$\beta = 93.360(7)$
Z, V (Å^3)	4, 1160.0(2)
D_c (g/cm^3)	3.424
μ (mm^{-1})	19.549
Completeness to theta = 27.51	99.9%
GOF on F^2	0.876
R_1, wR_2 ($I > 2\sigma(I)$)[a]	0.0191, 0.0386
R_1, wR_2 (all data)	0.0204, 0.0390
absolute structure parameter	0.007(5)
extinction coefficient	0.00582(9)
largest diff. peak and hole (e Å^{-3})	1.081, –0.665

[a] $R_1 = F_o - F_c / F_o$ and $wR_2 = [w (F_o^2 - F_c^2)^2 / wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma (F_o^2)$

Table S3 Atomic coordinates, isotropic displacement parameters, bond valence sums and global instability index (GII) for $Li_4HgGe_2S_7$.

atom	x	y	z	δ_{iso}	BVS[16,17]
Hg1	3768(1)	1320(1)	5525(1)	24(1)	2.077
Ge1	7312(1)	3368(1)	3282(1)	12(1)	4.008
Ge2	5211(1)	1767(2)	2621(1)	12(1)	4.036
S1	6276(1)	1696(2)	4122(1)	14(1)	1.979
S2	6992(1)	6429(2)	2951(1)	16(1)	2.025
S3	5473(1)	3316(2)	839(1)	19(1)	2.103
S4	7655(1)	1686(2)	1548(1)	16(1)	2.059
S5	4224(1)	3260(2)	3539(2)	16(1)	2.028
S6	4930(1)	-1377(2)	2232(2)	16(1)	2.083
S7	8257(1)	2949(2)	4865(1)	16(1)	2.143
Li1	6572(8)	-1940(20)	4851(13)	16(2)	1.057
Li2	8025(11)	1650(20)	7056(19)	24(3)	1.086
Li3	4455(10)	6790(19)	4055(18)	17(2)	1.106
Li4	5919(11)	6530(20)	1260(19)	28(4)	1.044
		GII[18-20]			0.073

In order to ensure the reasonability of crystal structures of these compounds, bond valence and Global Instability Index (GII) are systemically calculated (Table S2). The method of bond-valence parameters was used to calculate the bond valences of elements. The following equation is commonly used to calculate the bond valence (v_{ij}):

$$V_i = \sum_j v_{ij} = \sum_j \exp\left(\frac{r' - r_{ij}}{B}\right)$$

Where r' is empirically determined bond valence parameter, r_{ij} is actual bond length, and B is commonly taken to be a universal constant equal to 0.37 Å. Calculated results (Li, 1.044−1.106; Hg, 2.077; Ge, 4.008−4.036; S, 1.979−2.143) indicate that all atoms are in reasonable oxidation states. In addition, GII can be derived from the bond valence concepts, which represent the tension of lattice parameters and always used to evaluate the rationality of structure. While the value of GII is less than 0.05 vu (valence unit), the tension of structure is not proper, whereas the value of GII is larger than 0.2 vu, its structure is not stable. Thus, the value of GII in a reliable structure should be limited at 0.05−0.2 in general. As for $Li_4HgGe_2S_7$, calculated GII value is 0.073 vu, which illustrates that its crystal structure is reasonable.

Table S4 LDTs of $Li_4HgGe_2S_7$ and $AgGaS_2$ (as the reference)

compounds	damage energy (mJ)	spot diameter (mm)	LDT (MW/cm^2)
$AgGaS_2$	0.58	0.5	29.6
$Li_4HgGe_2S_7$	2.04	0.5	104.0

Table S5 Calculative polyhedral dipole moments for $Li_4HgGe_2S_7$.

Units	*x*	*y*	*z*	debye
HgS_4	0.66	0.00	1.03	1.19
$Ge1S_4$	−1.16	0.00	10.55	10.69
$Ge2S_4$	−0.15	0.00	2.98	3.00
Unit cell	4.33	0.00	17.08	17.38

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